

**Rentran Translation Services**

Gerd and Kathy Renno  
3067 N. Fennimore Ave.  
Tucson, AZ 85749-8189  
Phone: (520) 760-8468  
Fax: (520) 574-8687  
E-mail: gkrenno@cox.net

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(71) Applicant: Akademie der Wissenschaften der DDR (Academy of the Sciences of the GDR), Otto-Nuschke-Straße 22-23, Berlin, 1080, DD

(72) Inventor: Haberland, Egbert, Dipl.-Stomatologe; Hertzog, Klaus, Dr. rer. nat.; Schülke, Ulrich, Dr. rer. nat., DD

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(54) Phosphorous-containing adhesion promoter

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(55) Phosphorous-containing adhesion promoter, adhesive strength, methacrylate adhesive, methacrylate coating, polyvinyl chloride adhesive, polyvinyl-chloride coating, bonded materials, N-acryloyl-amino-methane-bisphosphonic acid, bonds, physiologically compatible salts, water soluble alkali salts, water soluble alkaline earth salts

(57) The invention concerns a phosphorous-containing adhesion promoter for increased bond strength of bonds with methacrylate adhesives or coatings, or polyvinyl chloride adhesives or coatings. Bonded materials include metals, organic polymers, ceramics, and glasses, as well as filler materials, and also hard, living tissue such as bones and teeth bonded with and among each other. The adhesion promoter of the invention contains 0.01 to 10 % wt. of an N-acryloyl-amino-methane- bisphosphonic acid or its salt of the general formula per above description in an aqueous solution. The adhesion promoter for

methacrylate bonds with hard, human tissue contains 0.01 to 10 % wt, preferably 0.1 to 2 %wt, of the N-acryloyl-amino-methane-bisphosphonic acid or its physiologically acceptable salts (water-soluble alkali or alkaline earth salts) in an aqueous solution.

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5 pages

- 1 -

## Patent Claims

1. Phosphorous-containing adhesion promoter for increased bond strength of bonds with methacrylate adhesives or coatings, or polyvinyl chloride adhesives or coatings, **characterized by** the adhesion promoter containing 0.01 to 10 % wt of an N-acryloyl-amino-methane-bisphosphonic acid of the general formula

*(See formula on original)*

in which  $R^1$  is -H, -OH, or an alkyl rest with 1 to 5 C-atoms,  $R^2$  represents -H, or an alkyl rest with 1 to 5 C-atoms, and n is a whole number between 0 and 5, or its salts in an aqueous solution.

2. Phosphorous-containing adhesion promoter for increased bonding strength of bonds with methacrylate adhesives according to Claim 1 with hard, human tissue, **characterized by** the adhesion promoter containing 0.01 to 10 % wt. of an N-acryloyl-amino-methane-bisphosphonic acid, or its physiologically acceptable salts in an aqueous solution.

3. Phosphorous-containing adhesion promoter according to Claim 2, **characterized by** it containing 0.1 to 2 % wt. of an N-acryloyl-amino-methane-bisphosphonic acid or its physiologically acceptable salts in an aqueous solution.

4. Phosphorous-containing adhesion promoter according to Claims 2 and 3, **characterized by** the physiologically acceptable salts being aqueous alkali or aqueous alkaline earth salts.

5. Method for increasing the bond strength of methacrylate adhesive bonds with hard, human tissue, **characterized by** applying to a pretreated surface, which is to be bonded on the hard, human tissue, and on the other bonding material, prior to the methacrylate bonding  
- an adhesion promoter in an aqueous solution consisting of 0.01 to 10 parts by weight in % N-acryloyl-amino-methane-bisphosphonic acid of the general formula

*(Formula)*

in which R<sup>1</sup> is -H, -OH, or an alkyl rest with 1 to 5 C-atoms, R<sup>2</sup> represents -H, or an alkyl rest with 1 to 5 C-atoms, and n is a whole number between 0 and 5, or its physiologically acceptable salts, or

- a dried and milled mixture of the adhesion promoter and a filler material mixed with the adhesive polymer.

6. Method according to Claim 5, **characterized by** applying

- an adhesion promoter consisting of 0.1 to 2 parts by weight in % of the N-acryloyl-amino-methane-bisphosphonic acid, or its physiologically acceptable salts in aqueous solution, or

- a dried and milled mixture of said adhesion promoter and a filler mixed with the adhesive polymer.

7. Method according to Claims 5 and 6, **characterized by** preparing the mixture of adhesion promoter and filler at a mass ratio of adhesion promoter to filler of 0.1 to 100 up to 10 to 100, preferably of 2 to 100.

8. Method according to Claims 5 to 7, **characterized by** the physiologically acceptable salts being aqueous alkali or aqueous alkaline earth salts.

- 2 -

### **Application of the invention**

The invention concerns a phosphorous-containing adhesion promoter for increasing bonding strength in bonds with methacrylate adhesive or coatings, or with polyvinyl chloride adhesive or coatings. The materials to be bonded are metals, organic polymers, ceramics, and glasses, as well as filler materials, and also hard, living tissue such as bones and teeth bonded with each other and among each other.

### **Characteristics of the known state of the art**

A number of adhesion promoters and adhesive coatings have already been developed and described to improve the adhesion between bonded materials.

Especially esters of the phosphoric acid, which contain vinyl, acryloyl, or other unsaturated groups in the organic rest, have been described for use in stomatology over the last few years, for example, in Euro-PS 0 058 483, Euro-PS 0 074 708 and Euro-PS 0088527 A2. The use of phosphoric or phosphonic acid esters with multiple C-C bonds in the organic part of the molecule as adhesion promoter between bonding resins and dental material (dentine and/or enamel) is practiced, for example, according to US-PS 4259075 and US-PS 4368043. According to US-PS 4525493, diphosphonic acids with the group

*(Formula)*

whereby  $-R^1$  and  $R^2$  stand for organic rests with at least one multiple C-C bond, are utilized for the same application.

However, most products of this kind are not hydrolysis resistant to a sufficient degree, especially under the conditions present in the mouth cavity, that is to say, constant exposure to saliva liquids at changing temperatures (changes by about 40 K) and pH conditions. Phosphonic-acid derivatives exhibit improved hydrolysis resistance, and their application as adhesion promoter for the adhesion of hard, human tissue is described in DE-OS 2 818 068, whereby average tensile strength values of 7.3 MPa are achieved in bonds of ivory with acrylates.

The similar is valid for the application of 1-methacryloxy-ethane-1,1-bisphosphonic acid described in DE-OS 3 150 285 A1, whereby the bond strength in this case also leaves something to be desired.

### **Goal of the invention**

The goal of the invention is to provide a new phosphorous-containing adhesion promoter with increase bond strength, even under physiological conditions, which consists of a starting substance that can be relatively easily obtained, and can be applied without organic solvents.

### **Description of the nature of the invention**

The underlying task of the invention is to develop an adhesion promoter according to the goal of the invention from derivatives of amino-methane-bisphosphonic acid for bonds with methacrylate adhesives or coatings, or polyvinyl chloride adhesives or coatings.

The phosphorous-containing adhesion promoter of this invention contains 0.01 to 10 %wt of N-acryloyl-amino-methane-bisphosphonic acid of the general formula

*(See formula in original)*

in which  $R^1$  is  $-H$ ,  $-OH$ , or an alkyl remainder with 1 to 5 C-atoms,  $R^2$  represents  $-H$ , or an alkyl rest with 1 to 5 C-atoms, and  $n$  is a whole number between 0 and 5, or its salts in an aqueous solution.

For methacrylate adhesives with hard, human tissue, the adhesion promoter according to the invention contains 0.01 to 10 % wt, preferably 0.1 to 2 %wt, of N-acryloyl-amino-methane-bisphosphonic acid, or its physiologically acceptable salts in an aqueous solution. Physiologically acceptable salts are aqueous alkali or aqueous alkaline earth salts.

- 3 -

The application of the phosphorous-containing adhesion promoter is carried out such that either the adhesion promoter containing 0.01 to 10 % wt, preferably 0.1 to 2 % wt, of the N-acryloyl-amino methane bisphosphonic acid or its physiologically acceptable salts in an aqueous solution, or a dried and milled mixture of adhesion promoter and filler mixed with adhesive polymer, is applied prior to the methacrylate adhesive bonding to the pretreated surfaces of the hard, human tissue and the other adhesive material, which are to be bonded. The mixture of adhesion promoter and filler is prepared according to the invention at a mass ratio of 0.1 to 100 up to 10 to 100, preferably at 2 to 100.

The phosphorous-containing adhesion promoter of this invention is characterized by the following advantages:

1. Superior bond strength of an average of 16 MPa, which is also maintained over a long period of time in a biological environment (temperature change, hydrolysis, mechanical stress, etc.).
2. Excellent bio-compatibility
3. Problem-free application, because the components of the invention can be incorporated into the adhesive polymer.
4. The excellent water solubility of the components of this invention requires no organic solvent.
5. Simple production of the starting materials and of the N-acryloyl-amino-methane-bisphosphonic acid.

The production of the N-acryloyl-amino-methane-bisphosphonic acid occurs in known manner by conversion of the corresponding acryloyl-chloride with amino-alkane-bisphosphonic acid in alkaline solution.

The invention is described by the following design examples in detail without being limited to them.

## **Design examples**

### **Example 1**

Production of N-acryloyl-amino-methane-bisphosphonic acid

1 mol amino-methane-bisphosphonic acid is dissolved in a solution of 3.2 mols  $K_2CO_3$  in 500 ml of water; 1 mol of the acryloyl-chloride (for example, acrylic acid chloride) is added in drops while cooling on ice, whereby the temperature shall not exceed 283 K. After acidifying with hydrochloric acid, the free bisphosphonic acid can be obtained from the solution by ion exchange or by crystallization as potassium salt.

## Example 2

A primer preparation is prepared by dissolving N-acryloyl-amino-methane-bisphosphonic acid in distilled water at a concentration of 1 part by weight in %. An enamel sample from cattle and a cube of a nickel-chrome alloy are polished with the help of a wet polishing device to a 600-grain polish.

The polished surface of the cattle tooth is treated for 30 seconds with a 37% ortho-phosphoric acid solution, blown off for 20 seconds with oil-free, compressed air and dried. The nickel-chromium alloy is sandblasted with  $Al_2O_3$  corundum (grain size 400  $\mu m$ , 20 seconds at 0.5 MPa jet pressure at a distance of 5 cm from the jet nozzle).

Then the produced primer is applied to the dried surface, left there to soak in for at least 30 seconds, and then blown off and dried. Afterwards, the solid materials are brought into contact while applying an adhesive polymer of the composition below. The entity is stored for one day and 30 days in artificial saliva at a temperature of 37° C, or in a temperature cycle device for 1,440 cycles (one cycle = 30 seconds in a bath at 18° C and 30 seconds in a bath at 60° C). The pressure-shear strength is tested after storage with a pressure-testing device at a traverse velocity of 0.5 mm/minute. The results obtained are summarized in Table 1.

## Composition of the adhesive polymer

A	Weight Parts	B	Weight Parts
Bisphenol-A-diglycidyl-methacrylate (Bis-GMA)	16.7	Silane-coupled inorganic filler	69.6
Tri-ethylene-glycol-dimethacrylate (TEGMA)	7.1	Bis-GMA	4.3
N,N-di( $\beta$ -hydroxy-ethyl)-p-toluidine	0.2	TEGMA	1.9
		Benzoylperoxide (Silane: Metharyloxypropyltri-methoxy-silane), Filler: pyrogenic $SiO_2$	0.2

Component (A) and (B) are mixed immediately before their application at a weight ratio of 24:76 and immediately used as adhesive polymer.

**Table 1**

Bond strength in MPa		
1 day	30 days	1,400 cycles
16.0	14.0	14.3

### Example 3

100 parts by weight of hydroxyl-atpatite or similar filler are mixed with 200 parts by wt. of the primer preparation of Example 2, and are dried at 120° C while continuously stirring. The obtained filler is milled with a ball mill and mixed with a polymer adhesive of the composition following below. The cattle enamel and Ni-Cr alloy surfaces polished and conditioned according to Example 2 are brought into contact while using this opaque adhesive material. The pressure shear strength is measured after storage as in Example 2. The results obtained are summarized in Table 2.

- 4 -

### Composition of the adhesive polymer

A	Weight Parts	B	Weight Parts
Bis-GMA	16.7	Silane-coupled inorganic filler	43.3
TEGMA	7.1	Bis-GMA	2.7
N,N-di(β-hydroxy-ethyl)-p- toluidine	0.2	TEGMA	1.9
		Benzoyl-peroxide	0.2
		OHAp + primer preparation	27.9

Components (A) and (B) are immediately mixed before their application at a weight ratio of 24:76 and immediately applied as adhesive polymer.

**Table 2**

Bond strength in MPa		
1 day	30 days	1,400 cycles
16.0	15.6	16.0

As can be seen from Table 2, the cured component according to this invention maintains its superior bond strength over a long time.

### Example 4

Two flat Ni-Cr test samples, sandblasted according to Example 2, are brought into contact using the adhesive preparation according to Example 3. The pressure-shear strength is measured after storage according to Example 2, and the results are summarized in Table 3.

**Table 3**

Bond strength in MPa		
<b>1 day</b>	<b>30 days</b>	<b>1,400 cycles</b>
19.0	18.8	19.0